

High-Resolution Pulsed Field Ionization Photoelectron-Photoion Coincidence Study of C_2H_2 : Accurate 0 K Dissociation Threshold for C_2H^+

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INTRODUCTION

The VUV photoelectron-photoion coincidence (PEPICO) method is the combination of these techniques, which involves the detection of correlated photoelectron-photoion pairs. The ion-internal-energy selection achieved in a PEPICO experiment depends critically on the photoelectron detection scheme used. Pulsed field ionization (PFI)-photoelectron (PFI-PE) spectroscopy, which relies on the detection of electrons formed at slightly below the true ionization threshold by PFI of high- n ($n \geq 100$) Rydberg species, is shown to be free from the hot-tail problem in previous laser-based studies. Taking advantage of the high-resolution capability of the Chemical Dynamics Beamline at the Advanced Light Source (ALS), we have developed PFI-PE detection schemes for multibunch measurements, achieving routinely resolutions in the range of $1\text{--}5\text{ cm}^{-1}$ (FWHM). Most recently, we have further developed the PFI-PEPICO method for use with both two-bunch and multibunch synchrotron radiation at the ALS, attaining a resolution of 0.6 meV (FWHM), limited only by the PFI-PE measurement.

In this study, we report on the application of this PFI-PEPICO method for the study of the formation of ethynyl ion (C_2H^+) from acetylene (C_2H_2), $C_2H_2 + h\nu \rightarrow C_2H^+ + H + e^-$, which is known to be a prompt dissociation process. Furthermore, this experiment provides evidence that $C_2H_2^*$ fragments into $C_2H^* + H$ prior to field ionization, where $C_2H_2^*$ (C_2H^*) represents C_2H_2 (C_2H) in high- n Rydberg states. The C_2H radical is believed to play a significant role in soot formation in flames and the hydrocarbon balance in planetary atmospheres. For this reason, the accurate establishment of the thermochemical cycle for the C_2H/C_2H^+ system is important.

EXPERIMENT

All measurements were made using the newly developed PFI-PEPICO apparatus and dispersed multibunch synchrotron radiation from the ALS. In the multibunch operation, the ALS period (656 ns) consists of 256 micro-VUV bunch (bunch width = 50 ps, separation of adjacent bunches = 2 ns) followed by a dark gap (light off period) of 144 ns. In this study, the PFI pulse (height = 7.0 V/cm , width = 200 ns) was applied approximately 10 ns after the start of the dark gap. Since the dark gap was only 144 ns in duration, some overlap with the light occurs. A dc field of 0.2 V/cm is maintained across the interaction region to sweep prompt electrons from the ionization region prior to the application of the electric field pulse for Stark ionization. The PFI-PE selection was achieved by employing the electron TOF scheme. The ion PFI-PEPICO TOF spectra were recorded using a multichannel scaler triggered by the detection of an electron. The photon energy ($h\nu$) calibration was achieved using the PFI-PE bands for $Ne^+(^2P_{3/2})$ and $Ar^+(^2P_{3/2})$ recorded under the same experimental conditions before and after each scan.^{13,14} This calibration procedure assumes that the Stark shift for ionization thresholds of C_2H_2 and the rare gases are identical. On the basis of the measured PFI-PE band for $Ar^+(^2P_{3/2})$, we estimate that the ion-energy selection achieved here is $\approx 1.0\text{ meV}$ (FWHM).

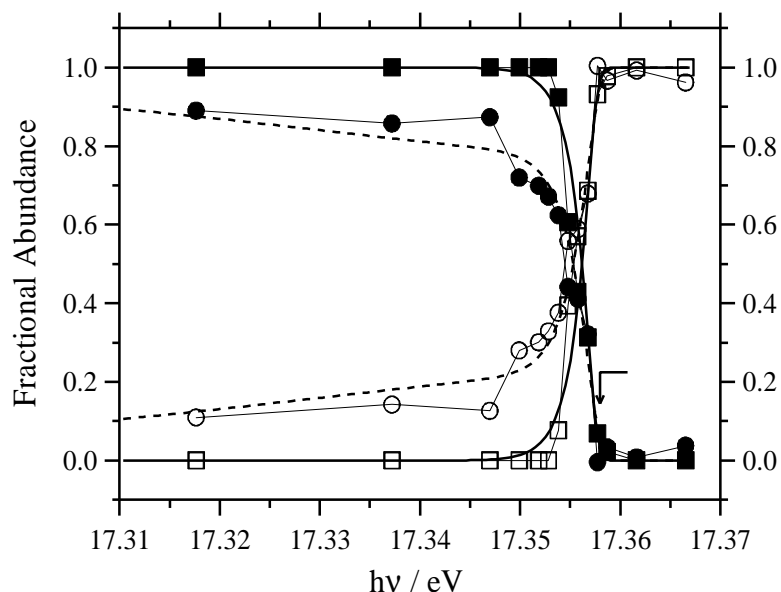


Figure 1. Breakdown curves of C_2H^+ and C_2H_2^+ in the $h\nu$ range of 17.31-17.37 eV. The experimental fractional abundances for C_2H^+ and C_2H_2^+ obtained based on the entire daughter ion signal are (\square) and (\blacksquare), whereas those obtained using only the cold daughter ion signal are indicated as (\circ) and (\bullet), respectively. The lines are simulation curves: (—) 20 K ensemble and (---) 20 K ensemble with 15% thermal background and with an energy dependent loss. See the text.

RESULTS AND DISCUSSION

We have obtained PFI-PEPICO TOF spectra for C_2H^+ and C_2H_2^+ in the $h\nu$ region of 17.2688-17.3959 eV, which is near the C_2H^+ dissociation threshold. We have simulated the individual TOF spectra using two Gaussian functions to account for the respective contributions due to the cold beam and thermal background C_2H_2 sample. Since the PFI-PEPICO TOF spectra resolve the dissociation due to cold C_2H_2 from that of thermal C_2H_2 , we have analyzed the TOF spectra by taking into account only the ‘cold’ C_2H^+ ion signal based on the narrow TOF component. Due to the efficient rotational cooling of C_2H_2 achieved by the supersonic expansion, the ‘cold’ breakdown curves thus obtained are very sharp as indicated by open and solid squares for the respective fractional abundances of C_2H^+ and C_2H_2^+ shown in Fig. 1. We have also constructed the breakdown curves for C_2H^+ and C_2H_2^+ [see open and solid circles, respectively, in Fig. 1] by including the total ‘hot’ and ‘cold’ C_2H^+ signals. We have performed simulation of the breakdown curves using similar procedures described previously. All calculations were based on rovibronic densities of states taking into account one two-dimensional rotor. The vibrational densities of states were calculated by the Beyer-Swinehardt algorithm based on known harmonic frequencies. By assuming a temperature of 20 K for C_2H_2 in the molecular beam, we have obtained an excellent simulation (solid lines) of the ‘cold’ breakdown curves, yielding a value of 17.3576 ± 0.0010 eV for the 0 K dissociation threshold of C_2H^+ from C_2H_2 . The dashed lines in Fig. 1 are calculated breakdown curves assuming 15% thermal background in addition to the 20 K cold beam discussed above. As in the case of the methane dissociation to form CH_3^+ , in order to obtain good fit to the breakdown curves, which include the dissociation of thermal C_2H_2 , we need to take into account the loss of parent C_2H_2^* due to spontaneous autoionization.

A most interesting observation is that the fraction of fragmentation due to the ‘hot’ C_2H_2 sample is considerably higher than the estimated 15-25% for the thermal background contribution to the experimental C_2H_2 sample. The observation of this effect can be rationalized by a competition between autoionization and fragmentation of C_2H_2^* at energies below and above the dissociation threshold. If the ion core C_2H_2^+ of C_2H_2^* is dissociative with a lifetime shorter than the delay time between the excitation micro-VUV pulse for the formation of C_2H_2^* and the electric field pulse for PFI, a viable mechanism for the formation of C_2H^+ from C_2H_2^* is



According to this mechanism, C_2H_2^* first undergoes prompt dissociation to form $\text{C}_2\text{H}^* + \text{H}$. The subsequent PFI of C_2H^* results in the formation of C_2H^+ and a PFI-PE. The recent lifetime measurements²⁴ of O_2 in high- n Rydberg states (O_2^*) converging to dissociative O_2^+ states provide strong support for process (1) as the major process for C_2H^+ formed in the PFI of C_2H_2^* . We note that any high- n Rydberg species, which have spontaneously autoionized before the application of the pulsed electric field, are lost to the PFI detection. The C_2H^* radicals formed by fragmentation of C_2H_2^* at the dissociation threshold are expected to form below the IE of C_2H . Thus, autoionization is not readily accessible for C_2H^* and is predominantly operative for C_2H_2^* , which lies at energies far above the IE of C_2H_2 . For C_2H^* formed slightly above the dissociation threshold, it can also autoionize. However, the autoionization of this C_2H^* may still be less probable than that of C_2H_2^* . The higher than expected PFI-PEPICO intensity for C_2H^+ from thermal C_2H_2 observed below the dissociation threshold can thus be accounted for by a longer autoionization lifetime for C_2H^* than that for C_2H_2^* .

Taking into account the experimental uncertainties, the dissociation threshold (17.3576 ± 0.0010 eV) for C_2H^+ from C_2H_2 determined here is consistent with values obtained in previous photoion and PEPICO studies. However, the value obtained here is characterized by a significantly higher accuracy. The combination of the well-known IE (C_2H_2) and the 0 K dissociation threshold for C_2H^+ from C_2H_2 determined here yields $D_0(\text{H}-\text{C}_2\text{H}^+) = 5.9570 \pm 0.0012$ eV. By combining the 0 K dissociation threshold for process (1) and the known $D_0(\text{H}-\text{C}_2\text{H})$ value, we calculate a value of 11.6451 ± 0.0014 eV for IE (C_2H). Using the well-established ΔH°_{f0} values for C_2H_2 and H, we also obtain $\Delta H^\circ_{f0}(\text{C}_2\text{H}^+) = 1694.44 \pm 0.80$ kJ/mol. We note that the accuracy of the latter value is now limited by the $\Delta H^\circ_{f0}(\text{C}_2\text{H}_2)$.

SUMMARY

By employing the newly developed pulsed field ionization photoelectron-photoion coincidence (PFI-PEPICO) apparatus of the Chemical Dynamics Beamline at the Advanced Light Source, we have examined the formation of ethynyl ion (C_2H^+) from acetylene (C_2H_2) at high resolution. The PFI-PEPICO time-of-flight spectra reveal that fragmentation of C_2H_2 in high- n Rydberg states occurs at energies above the dissociation threshold prior to pulsed field ionization. This study shows that for a prompt dissociation process, the disappearance energy of the parent molecule determined in PFI-PEPICO measurements provides an unambiguous measure of the 0 K ion dissociation threshold. For the formation of C_2H^+ from C_2H_2 this is found to be 17.3576 ± 0.0010 eV.

REFERENCE

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